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Electron Microscopy Studies of Potential 1-eV Bandgap Semiconductor Compounds $ZnGeAs_2$ and Zn_3As_2 Grown by MOVPE

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A.G. Norman, J.M. Olson, M.J. Romero, and M.M. Al-Jassim

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National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Electron Microscopy Studies of Potential 1-eV Bandgap Semiconductor Compounds $ZnGeAs_2$ and Zn_3As_2 Grown by MOVPE

A. G. Norman, J. M. Olson, M. J. Romero, and M. M. Al-Jassim
National Renewable Energy Laboratory (NREL)
1617 Cole Boulevard, Golden, CO 80401

ABSTRACT

We have performed electron microscopy studies on metal-organic vapor phase epitaxy (MOVPE) layers of $ZnGeAs_2$ and Zn_3As_2 that are potential 1-eV bandgap semiconductors for multijunction solar cells lattice-matched to GaAs and InP substrates, respectively. Epitaxial chalcopyrite $ZnGeAs_2$ on GaAs substrates was obtained only for a very narrow range of growth conditions. Under different growth conditions, epitaxial layers of the body-centered tetragonal structure Zn_3As_2 compound was obtained that is lattice-mismatched to the GaAs substrate, and hence contained a high density of threading defects such as dislocations.

1. Introduction

The addition of a good electrical-quality 1-eV junction in the present record-efficiency GaInP/GaAs/Ge cascade solar cell is expected to lead to a significant improvement in the overall efficiency of the device [1]. $ZnGeAs_2$ has the chalcopyrite structure with a = b = 0.567 nm and c = 1.115 nm [2], and so is very nearly lattice-matched to (001) GaAs and Ge substrates. It is believed to exhibit a direct bandgap at room temperature of ≈ 1.15 eV [2], making it a good candidate semiconductor material for the extra 1-eV junction. However, it may only be grown epitaxially by MOVPE on GaAs under a very narrow range of growth conditions [2]. Under different growth conditions, the body-centered tetragonal structure Zn_3As_2 compound is obtained [2] that is lattice-mismatched to GaAs, but close to lattice-matched to (001) InP substrates [3, 4]. This compound also has a bandgap of close to 1 eV at room temperature [3-5] making it of potential interest for multijunction solar cell applications. In this paper we will report the results of recent electron microscopy studies of MOVPE layers of these compound semiconductors grown at NREL.

2. Experimental

The layers studied in this work were grown by low-pressure (50 Torr) MOVPE, using arsine, germane, and diethylzinc as sources. Layers were grown on top of thin lattice-matched $Ga_{0.52}In_{0.48}P$ buffer layers on 6°B offcut (001) GaAs substrates over a range of growth temperatures using a Zn/Ge source flow ratio of ≈ 5. Transmission electron microscopy (TEM) and diffraction (TED) were used to examine the structure of the layers. Chemical analysis of the layers was performed using energy dispersive x-ray microanalysis (EDX). Optical properties of the layers were measured using cathodoluminescence (CL) at a temperature of 77 K in a scanning electron microscope.

3. Results

Fig. 1 shows a [110] high-resolution cross-section TEM image of a layer grown at ≈ 506°C. EDX analysis revealed no Ge in the layer, but Zn and As were present with a concentration ratio of about 3:2. TED patterns from the layer revealed an array of spots consistent with the layer being formed of the body-centered tetragonal structure Zn_3As_2 compound as reported previously for both MOVPE and MBE layers [2-4]. This compound grew epitaxially on the GaInP buffer layer despite an ≈ 4% lattice mismatch, as shown in Fig. 1. The interface, however, was rough, and a high density of misfit and threading dislocations resulted from the large lattice mismatch. A doubling in periodicity of the {111} plane lattice fringes is observed in the Zn_3As_2 layer in comparison to the zinc-blende substructure, as observed previously by other workers in lattice images of the Zn_3As_2 compound [3, 4, 6]. The non-incorporation of Ge in this layer may be associated with the incomplete decomposition of germane at this growth temperature and the relatively high vapor pressure of the Zn as compared to the Ge [2].

CL spectra taken from this layer at 77 K using an accelerating voltage of 30 kV revealed a dominant luminescence peak at ≈ 1.045 eV with a weaker peak at 0.85 eV (Fig. 2, solid line). It is thought that the minimum bandgap of Zn_3As_2 is indirect in nature, and that the direct bandgap is only 20–30 meV higher in energy, falling in the range 0.99–1.02 eV at room temperature [3–5]. The highest energy peak observed is therefore close to both the previously reported indirect and direct bandgaps for this compound.

Increasing the growth temperature to ≈ 518°C, while

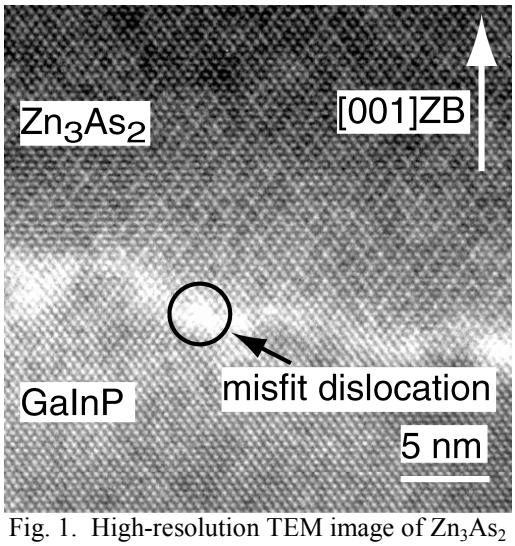

Fig. 1. High-resolution TEM image of Zn_3As_2 layer grown epitaxially on GaInP.

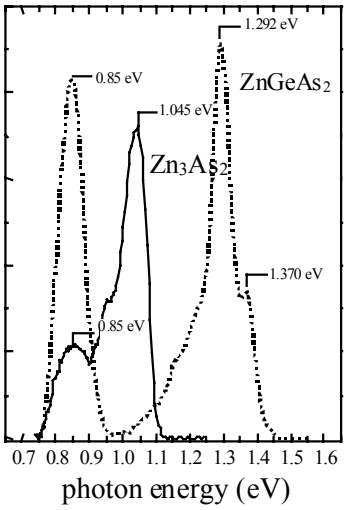

Fig. 2. 77 K CL spectra of Zn_3As_2 (solid line, E_b = 30 kV) and $ZnGeAs_2$ (dotted line, E_b = 15 kV) layers.

keeping the other growth conditions identical, resulted in the epitaxial growth of chalcopyrite $ZnGeAs_2$, close to lattice-matched to GaAs. EDX spectroscopy revealed the presence of Zn, Ge, and As in this layer with close to the expected ratios for $ZnGeAs_2$. TED results obtained from a plan view sample of this layer revealed the presence of an array of extra spots consistent with the presence of chalcopyrite $ZnGeAs_2$ (Fig. 3).

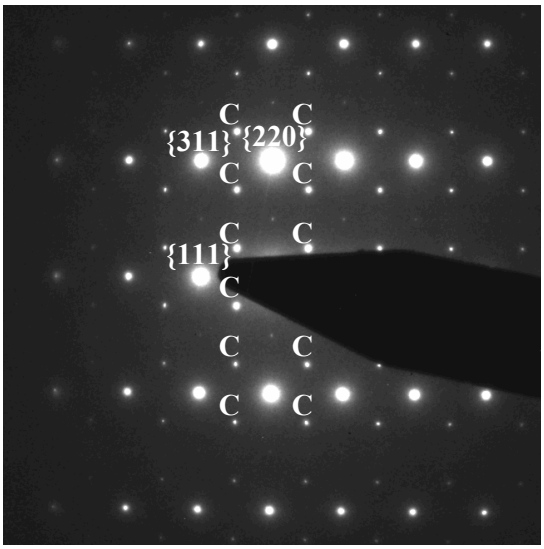

Fig. 3. TED pattern taken at [112] zinc-blende zone axis of GaAs substrate showing array of extra spots, e.g., labeled C, expected for chalcopyrite $ZnGeAs_2$ layer.

A 77 K CL spectrum taken from this sample at an accelerating voltage of 15 kV is shown in Fig. 2 (dotted line). Three peaks are present at energies of 1.37, 1.292, and 0.85 eV, with the peak at 1.292 eV being the most intense. The two highest energy peaks are significantly higher than the direct bandgap of ≈ 1.15 eV previously reported for MOVPE $ZnGeAs_2$ by Solomon et al. [2]. They are close in energy, however, to the dominant 80 K photoluminescence peak at 1.3 eV reported by Chelluri et al. [4] in MBE $ZnGeAs_2$ and the direct bandgap of 1.2 eV at low temperature recently calculated by Janotti et al. [7] for this compound.

4. Summary

We have successfully grown both chalcopyrite $ZnGeAs_2$ and body-centered tetragonal Zn_3As_2 epitaxial layers on (001) GaAs substrates using low-pressure MOVPE by careful control of the growth conditions. CL measurements indicate a 77 K bandgap of close to 1.05 eV for Zn_3As_2 and 1.37 eV for $ZnGeAs_2$.

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